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URANIUM DETERMINATION BY THE FISSION TRACK METHOD

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MICROMEDIA

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ABSTRACT

The Division of Nuclear Fuel Cycle of the International Atomic Energy Agency requested the participation of CANMET in the preparation of a manual of analytical methods for the uranium industry. The staff of the chemical laboratory has responded to this request and will issue several reports describing current methodology and laboratory practice. This report deals with the determination of uranium at trace and geological levels by the fission track method.

DÉTERMINATION DE L'URANIUM PAR LA MÉTHODE DE TRACES DE FISSION

par

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RÉSUMÉ

La Division du cycle du combustible nucléaire de l'Agence internationale de l'énergie atomique a demandé au CANMET de participer à la préparation d'un manuel de méthodes d'analyse à l'intention de l'industrie de l'uranium. Le personnel du Laboratoire de chimie a répondu à cette demande, et présentera plusieurs rapports décrivant la méthodologie et les méthodes d'analyse utilisées actuellement en laboratoire. Le présent rapport traite de la détermination de l'uranium au niveau de traces et au niveau géologique par la méthode de traces de fission.

INTRODUCTION

When a neutron enters the nucleus of an atom of uranium-235 the atom splits or "fissions" into two more-or-less equally massive smaller atoms ("fission fragments") which move apart at high velocities. When a fission fragment passes through a solid it breaks down the crystal lattice or molecules along its path producing a "fission track" (1). The material of a fission track differs from that of the unaltered solid around it in a number of ways and is, for example, more soluble. Thus fission tracks, which, when formed, are no more than 100Å in diameter, can be enlarged to a size visible through an optical microscope by exposing a surface through which they pass to a solvent in which the solid is slightly soluble. The fission tracks dissolve more rapidly than the surrounding solid and become pits of a size and shape which depend on the solid, length of exposure to the solvent and other factors. This process is known as track etching. Usually fission tracks are etched to a diameter of 10^{-4}-10^{-3} cm. Their length, as a rule, varies only with the solid, from $\sim 5 \times 10^{-4}$ cm to $\sim 30 \times 10^{-4}$ cm.

Only ^{235}U will fission by the "thermal" or "slow" neutrons used in neutron irradiations in nuclear reactors. The fraction of uranium which is U^{235} can be considered to be constant unless it has been altered by chemical or physical processes (as it has in many laboratory reagents). Therefore, if materials containing uranium are placed on an initially fission-track-and-uranium-free surface (this is usually a sheet of a plastic with the trade name of Lexan but sometimes clear, high-grade Muscovite mica is used), irradiated with neutrons in a nuclear reactor and the surface then etched, the number of fission tracks appearing on the surface depends only on the concentration of uranium in these materials and the number of neutrons (the neutron "fluence" or "dose") which passed through them. If one of the materials was a standard of known uranium concentration the concentrations of uranium in the others can be calculated by a simple proportionality.

When the samples to be analyzed are solids it is usual to place Lexan surfaces against them, irradiate, etch and determine with a microscope the "density" of tracks ρ (i.e. the number of tracks per square centimetre) on the Lexan opposite each solid.

$$\frac{[U]\ \text{Sample}}{[U]\ \text{Standard}} = \frac{\rho\ \text{Sample}}{\rho\ \text{Standard}}$$

The background of tracks due to uranium in the track detector may be determined by irradiating and etching surfaces that were placed against other track detectors. It is usually negligible when the track detector is Lexan. When muscovite is used the background is usually higher and muscovite usually contains "fossil" tracks before use which may be removed by heating for 1 hour at 550-600°C.

If the sample solid is homogeneous, a piece of it may be mounted in an epoxy disk, ground and polished to produce a surface against which the track detector can be placed. Inhomogeneous samples such as rocks and soils are ground and pressed into pellets (such as are used in X-ray fluorimetry) and the track detectors are placed against these (2,3). Standards which may be used repeatedly, are made in the same ways. Convenient standards for this method are now available from the National Bureau of Standards in Washington D.C., U.S.A. (SRM 610-617 and 961a-964a). Sample and standard disks covered with track detectors are stacked in an irradiation capsule, and irradiated with a suitable neutron dose in a nuclear reactor, after which the track detectors or "overlays" are removed and etched. Lexan is etched in 6M aqueous NaOH for about 24 hours, muscovite in 48% ("concentrated") HF for 15-60 minutes, both at room temperature. If the approximate uranium concentration in the samples is known, a suitable neutron dose, n, may be calculated from the formula:

$$\rho = (2)10^{-5}n[U]$$

where ρ is the "induced" fission track density (which should be about 10^{5}-10^{6} tracks per cm^2), [U] the weight fraction of uranium in the sample, and n is the neutron dose (neutron per cm^2). Hence, if [U] is 1 ppm a suitable neutron dose would be $(5)10^{15}$ n/cm^2 and, in a reactor with a neutron flux of 10^{13} $n/cm^2/sec$ the irradiation should be for 8-9 minutes. If it is believed that the neutron flux varies from point to point within the capsule during irradiation several standards may be placed in the capsule at different positions. Commercial aluminum foil is a convenient

secondary standard for this purpose: disks of it, covered with Lexan may be placed throughout a capsule (4).

Lexan or muscovite overlays may also be used to map the uranium concentrations in inhomogeneous solids, to locate the uranium-bearing minerals in a petrographic thin section or to learn if uranium and its radioactive decay products (located by other types of "autoradiography") have become separated (5).

The same technique may be used in the analysis of liquids (6,7,8), but it is usually more convenient to evaporate measured drops of a liquid sample on the Lexan surface, irradiate, etch, and determine T, the total number of tracks arising from the residue of each drop. The following relationship applies (9,10).

$$c = TM/VGN_A I\sigma n\varepsilon$$

Here c is in units of mass per mass, M is the atomic weight of the element whose isotope fissions, V is the volume of the water drop in millilitres, G is the fraction of the fission events which produce tracks in the detector, N_A is Avogadro's number, I is the fraction of the atoms of the element which are the fissioning isotope, σ is the cross section of this isotope in cm^2 for neutron-induced fission, n is the neutron dose in neutrons/cm^2, and ε is the efficiency with which the fission tracks become countable on etching. Where the element whose isotope fissions is uranium and the track detector is Lexan M = 238, G = 1, I = 0.0072, $\sigma = 5.82 \times 10^{-22}$ cm^2 and ε = 1. Using these values for the various terms, the equation becomes

$$c = 94.4T/nV$$

Using Lexan polycarbonate plastic as the detector, drop sizes of 0.05 or 0.005 mL and visual counting of the etched tracks, this method was used for measuring uranium concentrations of 10^{-11} or lower in natural waters. It was fast and inexpensive (3-6 minutes were required for track counting and as many as 1200 samples and standards could be irradiated in one capsule). Problems sometimes arose, however, apparently because chemicals in the solutions or other types of radiation present during the neutron irradiation affected the ability of the Lexan to record etchable fission

tracks (10). At present these effects are poorly understood. They would probably be completely absent if mica is used for the track detector (but even the best grade of muscovite contains much more uranium than Lexan) and they probably vary with the reactor used. In any case this method requires constant checking and recalibration which is easily carried out by including standard uranium solutions and "spiked" samples among the solutions being analyzed. In practice the uranium concentrations are calculated from the c to T relationship found from these and not from the theoretically derived relationship shown above. A person planning to use this method for measuring uranium in natural water should test both materials and procedures with standards before proceeding.

The formation of fission tracks is a random process and therefore the standard deviation in a count of T tracks should be $\sqrt{T}$, if there is no other source of variation and uncertainty in the determination. For this reason as many tracks as possible should be counted in every measurement. Other sources of error and uncertainty vary with the nature of the samples, procedures and other factors. One of these which needs comment is the error in recognizing fission tracks and distinguishing them from other features. In some materials etched fission tracks may vary considerably in appearance. Other features which, to some extent, resemble tracks may be present so that different analysts may report different numbers for tracks in the same area. This will not introduce systematic error if two rules are followed.

(1) Each analyst determines the c to T or c to ρ relationship from his own track counts on standards and uses this in converting his track counts for the samples to c.

(2) The track counter decides on criteria for distinguishing fission tracks from other features which insure that, although he may miss some real tracks, he will not count any other features. If he abides by the criteria he will always count some fixed fraction of the fission tracks. As the ultimate determination is based on the ratio of ρ or T for the sample to the standard, this factor cancels out.

The last rule assumes that the criteria or characteristics for distinguishing etched fission tracks from other features are the same for the samples as for the standards. This can be achieved when the tracks are

being counted in overlays placed on the samples and standards, and not in the sample and standard materials themselves.

The discussion to this point has assumed that the etched fission tracks are counted by eye with a microscope. For most uranium measurements this is entirely satisfactory. Powers of 150X to 600X are used, and the better grade of hobbyists' or student microscopes are adequate.

However, many instruments for counting etched particle tracks have been developed and probably more will appear in the future. The most widely used instrument is the discharge counter (11,12). Fission tracks are recorded by a Lexan film of such thickness (2-15 μm) that fission fragments pass through it. After etching, this film is placed between the two flat electrodes of the track counter. When a dc voltage of about 500 V is applied between these electrodes, discharges pass through the etched track holes. If one of the electrodes is a sheet of aluminized Mylar from which the discharges evaporate the aluminum, only one discharge passes through each track, and the number of discharges, recorded on a scaler, gives the number of tracks in the film.

Counting fission tracks by means of a discharge counter is fairly simple when the fission tracks are uniformly distributed over the track detector. This, of course, is the case when the sample and standard materials are homogeneous. If the uranium is inhomogeneously distributed throughout a sample however, (as when uranium-rich grains remain in powdered rocks), track clustering may occur in the detector. Adjacent and overlapping tracks etch as single holes and the number of discharges through the detector no longer bears a "reproducible" relationship to the number of fission tracks in it.

When inhomogeneity is a problem in the analysis of a solid, some means of homogenization must be found. The residues left by evaporating water droplets have been redistributed with sufficient homogeneity for fission track-discharge counter determination of their uranium by placing drops of diluted collodion on them (12). Such track clustering is less of a problem in visual track counting partly because the eye can distinguish the tracks in clusters better than an instrument and partly because a person counting tracks would recognize the clusters and know which analyses had been affected by them and how serious the effect might be.

The only other track counting instrument frequently referred to in the literature is the image analyser (13,14,15,16). When the appearance of the etched tracks can be controlled sufficiently, they may be used in routine track counting.

REFERENCES

1. Fleischer, R.L., Price, P.B. and Walker, R.M. "Nuclear tracks in solids, principles and applications"; University of California Press, Berkeley, Book, 605 + XXII pp.; 1970.

2. Fisher, D.E. "Homogenized fission track determination of uranium is whole rock geologic samples"; Anal Chem 42:414-416; 1970.

3. Stuckless, J.S., Millard, H.J. Jr., Bunker, C.M., Nkomo, I.J., Roshalt, J.N., Bush, C.A., Huffman, C. Jr., and Keil, R.L. "A comparison of some analytical techniques for determining uranium, thorium and potassium in granitic rocks"; J Res U.S. Geol Survey 5:81-91; 1977.

4. Aumento, F. "Uranium content of mid-oceanic basalts"; Earth Plan Sci Lett 11:90-94; 1971.

5. Dyck, W. and McCorkell, R.H. "A study of uranium-rich reduction spheroids in sandstones from Pugwash Harbour, Nova Scotia"; J Can Earth Sci 20:1738-1740; 1983.

6. Berzina, J.S., Popenko, D.P. and Shimelevich, Yu.S. "Determination of trace amounts of uranium in petroleum by means of fission tracks"; Geokhimiya, No. 8:1024-1027. Russian, English abstract. Translating available; see Geochem Internat 6:847, 1969.

7. Hashimoto, J. "Determination of the uranium content in sea water by a fission track method with condensed aqueous solution"; Anal Chim Acta 56:347-354; 1971.

8. Reimer, G.M. "Uranium determination in natural water by the fission-track technique"; J Geochem Expl 4:425-431; 1975.

9. Fleisher, R.L. and Lovett, D.B. "Uranium and boron content of water by particle track etching"; Geochim Consmochim Acta 33:1126-1128; 1968.

10. McCorkell, R.H. "A fission track method for determination of uranium in natural waters for geochemical exploration"; CIM Bulletin 76:852: 89-92; 1983.

11. Cross, W.S. and Tommasino, L. "A rapid reading technique for nuclear particle damage tracks in thin foils"; Rad Eff 5:85-89; 1970.

12. McCorkell, R.H. and Huang, Y.F. "Discharge counter for the determination of uranium in water by the fission tracks method"; Rev Sci Inst 48:1005-1009; 1977.

13. Carpenter, B.S. "Determination of trace concentration of boron and uranium in glass by the nuclear tracks technique"; Anal Chem 44:600-602; 1972.

14. Carpenter, B.S. "Quantitative applications of the nuclear track technique"; Microscope 20:175-182; 1972.

15. Carpenter, B.S. "Lithium determination by the nuclear track technique"; J Radioanal Chem 19:233-234; 1974.

16. Carpenter, B.S. and LaFleur, P.D. "Nitrogen determination in biological materials by the nuclear track technique"; Anal Chem 46:1112-1113; 1974.